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CLAIMS

(57) [Claim(s)]

[Claim 1] A general formula $R_1 - n \text{ Si}(\text{OR}_2)_n$ (R_1 and R_2 among a formula) expressing an aryl group which has independently an alkyl group which has 1-6 carbon numbers, or 6-10 carbon numbers, n expresses an integer of 2-4. At least two sorts chosen from organic silicon compounds expressed (however, two or more sorts chosen only from $\text{Si}(\text{OR}_2)_4$ and $\text{R}_1 - 2 \text{ Si}(\text{OR}_2)_2$ are removed.) In spreading liquid for silica system insulator layer formation which consists of a siloxane system prepolymer obtained by carrying out hydrolysis condensation, and an organic solvent Spreading liquid for silica system insulator layer formation characterized by for weight average molecular weight of this prepolymer being 2000-4000, and conductivity of this spreading liquid being 0.1 - 100 second/cm.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the spreading liquid for forming a silica system insulator layer on substrates, such as a semiconductor substrate, a metal plate, a glass plate, and a ceramic board. Furthermore, in detail, in case this invention forms a multilayer interconnection, it relates to the spreading liquid for silica system insulator layer formation which can carry out flattening of the level difference of the lower layer wiring with which the detailed pattern was formed.

[0002]

[Description of the Prior Art] In recent years, the demand about multilayer-interconnection technology is still more advanced with high integration of a VLSI. That is, the slot between patterns becomes narrow and the irregularity on the front face of an element is large, and when performing a multilayer interconnection, if the element surface irregularity formed with lower wiring (and insulator layer etc.) is large, it will be barred in exact formation of an up circuit pattern. For this reason, the flush-ized processing which loses the irregularity on the front face of an element has become indispensable. From such a viewpoint, the spreading film method flush nature was excellent in recent years has been improved.

[0003] There is much what is proposed by current as a spreading film. although things typical by the organic system are polyimide, polyimide silicone, etc. and these are excellent in crack-proof [flush nature and] nature -- thermal resistance, polish recon, aluminum and SiO₂, and Si₃ N₄ etc. -- it is inferior to adhesion with a base material (it may be called a "substrate" below), and there is a problem of the deterioration in a long period of time. It is a big defect that a solution happens in part at the temperature of 450 degrees C or more especially.

[0004] On the other hand, although the spreading film of the silica glass system which is the condensation polymerization object of a tetra-ethoxy silane is excellent in thermal resistance and adhesion with a substrate, it is inferior to crack-proof nature and there is an effect in relaxation of a certain amount of element surface irregularity, it cannot make flush the slot of narrow pattern width like the VLSI of a high degree of integration in recent years, or a high aspect ratio to the degree which does not have trouble in up circuit pattern formation.

[0005] On the other hand, although there is also a proposal of the composite of the poly RADA ORGANO siloxane, the poly RADA ORGANO siloxane, silica glass, etc., it is inferior to adhesion with a substrate, or crack-proof nature and membranous homogeneity, and is not practical (refer to JP,57-83563,A, JP,57-131250,A, and JP,56-129261,A.).

[0006]

[Problem(s) to be Solved by the Invention] In this actual condition, the technical problem which this invention person should solve is not based on the configuration of a pattern, but is to offer the polysiloxane system spreading liquid which can form the insulator layer which can carry out [flush]-izing of the level difference of lower layer wiring.

[0007]

[Means for Solving the Problem] Bases of a spreading film method dissolve base polymer which forms film in an organic solvent, are applied to a base material with immersion or a spin coat method, perform clearance and heat condensation polymerization of an organic solvent with heating, and consist of making a film of glassiness or a huge macromolecule form.

[0008] this invention persons are related with spreading liquid for silica system insulation coat which consists of a prepolymer obtained by condensation reaction of various organic silicon and an organic solvent. A result of wholeheartedly examination, With spreading liquid which consists of a thing and an organic solvent of a molecular weight range which is a prepolymer using a specific organic silicon compound And when it applied to an element front face where irregularity is big by adjusting conductivity of this spreading liquid, it found out crack-proof [flush nature and] nature being excellent, and becoming the good spreading liquid of conservation stability, and resulted in this invention.

[0009] That is, this invention is a general formula. (R1 and R2 among a formula) $R1-4-n Si(OR2)_n$ expressing an aryl group which has independently an alkyl group which has 1-6 carbon numbers, or 6-10 carbon numbers, n expresses an integer of 2-4. At least two sorts chosen from organic silicon compounds expressed (however, two or more sorts chosen only from $Si(OR2)_4$ and $R1-2Si(OR2)_2$ are removed.) In spreading liquid for silica system insulator layer formation which consists of a siloxane system prepolymer obtained by carrying out hydrolysis condensation, and an organic solvent Spreading liquid for silica system insulator layer formation characterized by for weight average molecular weight of this prepolymer being 1000 to 4000 or less, and conductivity of this spreading liquid being 0.1 - 100 second/cm is started.

[0010] As an organic silicon compound used for this invention, it is a general formula. $R1-4-n Si(OR2)_n$ (R1 and R2 express among a formula an aryl group which has independently an alkyl group which has 1-6 carbon numbers, or 6-10 carbon numbers, and n expresses an integer of 2-4.) What is expressed is used.

[0011] Among these, as an example of an organic silicon compound of $n=4$, 4 [i.e.,], functionality, a tetramethoxy silane, a tetra-ethoxy silane, tetra-isopropoxysilane, a tetra-phenoxy silane, etc. are raised. A tetramethoxy silane and a tetra-ethoxy silane are used especially suitably.

[0012] Next, as an example of an organic silicon compound of $n=3$, 3 [i.e.,], functionality, methyl trimetoxysilane, methyl triethoxysilane, a methyl triisopropoxy silane, methyl triphenoxysilane, ethyl trimethoxysilane, ethyltriethoxysilane, an ethyl triisopropoxy silane, ethyl triphenoxysilane, phenyl trimethoxysilane, phenyl triethoxysilane, a phenyl triisopropoxy silane, phenyl triphenoxysilane, etc. are raised. They are methyl trimetoxysilane, methyl triphenoxysilane, and methyl triethoxysilane preferably.

[0013] next, as an example of an organic silicon compound of $n=2$, 2 [i.e.,], functionality Dimethyl dimethoxysilane, dimethyl diethoxysilane, dimethyl diisopropoxysilane, A JIMECHIRUJI phenoxy silane, diethyl dimethoxysilane, diethyl diethoxysilane, Diethyl diisopropoxysilane, a JIECHIRUJI phenoxy silane, diisopropyl dimethoxysilane, Diisopropyl diethoxysilane, diisopropyl diisopropoxysilane, a diisopropyl JIFENOKI gardenia fruit run, diphenyl dimethoxysilane, diphenyl diethoxysilane, diphenyl diisopropoxysilane, a diphenyl JIFENOKI gardenia fruit run, etc. are raised. Dimethyl dimethoxysilane, dimethyl diethoxysilane, and diphenyl diethoxysilane are used especially suitably.

[0014] These organic silicon compounds carry out hydrolysis condensation of at least two or more (however, two or more sorts chosen only from $Si(OR2)_4$ and $R1-2Si(OR2)_2$ are removed.) sorts. $Si(OR2)_4$ from -- if spreading liquid is created by prepolymer which consists of two or more selected sorts, since an insulator layer heated and formed after applying on an element front face turns into a condensation polymerization object of a tetra-ethoxy silane described previously, and same silica glass film and is inferior to crack-proof nature, it cannot be used for flush-ization by VLSI of a high degree of integration.

[0015] On the other hand, an alkyl group and an aryl group remain in a final insulator layer by including an organic silicon compound of three functionality or two functionality, stress generated in a film at the

time of heating and cooling is eased, and it is thought that it becomes spreading liquid excellent in crack-proof nature. However, only with an organic silicon compound of two functionality, there are problems -- with a compound, it is liquefied or inferior to adhesion with a substrate -- and when using an organic silicon compound of two functionality, it uses combining an organic silicon compound of four functionality and/or three functionality.

[0016] What is necessary is just to choose an organic silicon compound in consideration of adhesion with construction material used as membrane quality as an insulator layer, or a substrate etc. according to a use to be used.

[0017] In using especially as an object for VLSIs, (a) 4 functionality organic silicon compound, (b) (a):(b):(c) = 0.05-0.8:0.03-0.8:0.07 3 functionality organic silicon compound and (c) 2 functionality organic silicon compound with a mole fraction Silicon substrate, It is desirable from adhesion with silicon oxide, a wiring material, etc., or membrane quality of a formed insulator layer, and (a):(b):(c) = 0.1-0.6:0.1-0.5:0.05-0.5 are more desirable.

[0018] In order to excel in embedding nature to a detailed (the GPC method, polystyrene conversion) pattern and to perform flush-ization of irregularity on a front face of an element, 1000-4000 are suitable for weight average molecular weight of a siloxane system prepolymer which carries out hydrolysis condensation of the above-mentioned organic silicon compound, and is obtained, and it is 2000-3000 preferably.

[0019] Next, a manufacturing method which obtains a low-molecular-weight siloxane system prepolymer of this invention is described.

[0020] Generally a hydrolysis polycondensation reaction of alkoxysilane is performed under existence of an acid catalyst or an alkali catalyst. Of course, an example carried out also under a non-catalyst is seen. A prepolymer of low molecular weight can be obtained by any method. In order to obtain a prepolymer of this invention with sufficient yield for a short time, an acid catalyst of a hydrochloric acid, a nitric acid, an acetic acid, etc. is desirable.

[0021] Reaction temperature is 150 degrees C or less, and is 0 degree C - 50 degrees C preferably.

[0022] A reaction method has a common method of mixing at least two sorts (except for two or more sorts chosen only from a thing of four functionality and two functionality) chosen from said organic silicon compound, and dropping and carrying out copolycondensation of the water. Although especially a solvent is not needed, aromatic series, such as ketones, such as ester, such as alcohols, such as a methanol, ethanol, and isopropanol, methyl acetate, ethyl acetate, and butyl acetate, a methyl ethyl ketone, and methyl isobutyl ketone, benzene, and toluene, can be used as a solvent. These become some solvents of spreading liquid as it is.

[0023] A catalyst may be supplied first and may be dropped together with water.

[0024] Its amount of 0.8 to 1.5 times of the amount of theories (it is one mol of water to an alkoxy group or two aryloxy groups) is desirable, and if they will form organic solvent insoluble matter in part by gelation if there are too many amounts of water, and there are, an alkoxy group or an aryloxy group as a non-condensed radical remains mostly and is not desirable [amounts]. [too few]

[0025] A batch process or continuous system may be used for this polymerization.

[0026] A method of obtaining suitable molecular weight of this invention stably somewhat interrupts a reaction for slight lowness from the target molecular weight, pursuing change of molecular weight by GPC. A method of interrupting a reaction removes a catalyst while diluting it with a solvent. Dilution by solvent is the object which only makes a reaction rate late, and the object is reached also by making temperature into 0 degree C or less.

[0027] Although various methods, such as a neutralization reaction, adsorption treatment, and ion exchange treatment, are taken, since a clearance method of a catalyst can ask for purity severely when using it for a semiconductor use, its clearance by ion exchange resin is desirable.

[0028] In order to also remove simultaneously mixed impurity metals, such as especially Na, and K and aluminum, it is desirable to carry out ion exchange treatment in a mixed bed of an anion exchange resin and cation exchange resin.

[0029] Next, spreading liquid for insulator layer formation is explained.

[0030] The above-mentioned siloxane system prepolymer is used dissolving so that thickness for which it asks to organic solvents, such as aromatic series system solvents, such as a monoalkyl ether system solvent of propylene glycols, such as a monoalkyl ether system solvent of ethylene glycol, such as ketones, such as ester solvents, such as alcohols solvents, such as a methanol, ethanol, and isopropanol, methyl acetate, ethyl acetate, and butyl acetate, an acetone, a methyl ethyl ketone, and methyl isobutyl ketone, and butyl Cellosolve, and 1-methoxy-2-propanol, benzene, and toluene, may be obtained.

[0031] In mixture of this siloxane system prepolymer and organic solvent, although concentration of this siloxane system polymer is suitably determined according to an operating condition, generally it is 4 % of the weight or more, and 20 or less are used suitably ten or more. It is easy to generate striae SHON on a film applied when it became 20% of the weight or more.

[0032] Next, the stability of the above-mentioned spreading liquid for insulator layer formation with the passage of time is described. If spreading liquid created by above-mentioned method remained as it was, even if it was carrying out cooling conservation, a property of spreading liquid changed within several days - one month, flattening of the irregularity on a front face of an element of a VLSI was carried out at the time of creation, and it became clear that flush nature and embedded nature were inferior in measuring it after also saving a thing excellent in a detailed pattern pad. Various examination showed that conductivity and relation of spreading liquid had stability with the passage of time.

[0033] That is, although conductivity of spreading liquid had flush nature sufficient also after several month conservation in the range and embedded nature of 0.1 - 100 second/cm, flush nature and embedded nature which spreading liquid after conservation excelled in conductivity at 0.1 or less second/cm and 100 second/cm or more were not shown. That is, conductivity of spreading liquid needs to manage to 0.1 - 100 second/cm, and its 0.2 - 30 second/cm is more desirable.

[0034] There is a method of controlling so that conductivity of spreading liquid serves as 0.1 - 100 second/cm before reacting an amount of an acid catalyst used for a reaction as a method of managing conductivity of spreading liquid. Moreover, as an option, there is a method of adding an acid which dissolves in spreading liquid, and a salt after removing a catalyst. Control is easy to carry out and is desirable if it adds dissolving an acid and a salt in an organic solvent component of spreading liquid as the addition method, and measuring conductivity of spreading liquid.

[0035] What is necessary is to dissociate in the condition of having dissolved and dissolved in an organic solvent used for spreading liquid, or alcohols generated at a reaction as an acid added in order to adjust conductivity, or a salt, although it may be partial, and just to be able to maintain conductivity of spreading liquid at 0.1 - 100 second/cm. The hydrogencarbonates of a hydrochloric acid, chlorides, an acetic acid and acetate, a nitric acid and nitrates, the phosphate of a phosphoric acid or a part, a chloric acid and chlorates, perchloric acid and perchlorates, a hydrobromic acid and bromides, and a hydroiodic acid and iodides part can be raised as such a thing.

[0036] Since it can ask for reduction of halogens metallurgy groups when using spreading liquid of this invention for a VLSI use especially, it is desirable to add an acid which does not contain them, or a salt. An acetic acid, ammonium acetate, acetic-acid tetramethylammonium, acetic-acid tetraethylammonium, carbonic acid hydrogen tetramethylammonium, a nitric acid, and an ammonium nitrate can be raised as such a thing.

[0037] Finally a formation method of an insulator layer is explained.

[0038] After it applies the above-mentioned insulator layer formation spreading liquid by a spin coat method or dip coating generally used first and an air dried or low-temperature heating subsequently removes a solvent enough, heat insulator layer formation in temperature of 400 degrees C or more, it makes an unreacted alkoxy group decompose, and is performed by making siloxane association form in this portion.

[0039] In this film formation, heat treatment is preferably performed more than for 30 minutes more than for 10 minutes, although it is dependent also on heat treatment temperature.

[0040]

[Example] An example explains this invention concretely below. Measurement of a physical-properties value was performed as following.

[0041] (1) the measurement GPC of weight average molecular weight (gel permeation chromatography) -- the value measured by law -- Shodex of Showa Denko K.K. Standard S It expressed with the polystyrene (bogey tube) reduced property using SL-105 of series. Measurement of the GPC method is TRIROTAR-III of Jasco Corp. as equipment. It is used and is Shodex of Showa Denko K.K. as a column. A-80M (8phix500mm) and/or KF-802 (8phix300mm) were connected, RI was used as a detector and ethyl acetate was used as an eluate. Moreover, the flow rate was considered as a part for 1ml/.

[0042] (2) It measured using the conductivity meter (CM-117 mold) of the measurement Kyoto electronic company of conductivity.

[0043] (3) It measured by non-contact using the nano spec. 210 of the measuring method nano metric company of thickness. It asked for the refractive index by the ellipsometry method, and it used the value.

[0044] (4) With H-Mikasa, Inc spinner 1 360 mold of spin coat method Mikasa, Inc, spreading liquid was dropped on several ml silicon, revolution spreading was carried out for 15 seconds by 500 - 3500rpm, and the spreading film was formed.

[0045] (5) With [of the thermal oxidation film a line and whose space width the measuring method level difference of whenever / flush-ized / is 0.6-2.0 micrometers in about 1 micrometer] a pattern N2 after forming a spreading film with a spin coat method on a 4 inch silicon wafer With the firing furnace of an ambient atmosphere, 450 degrees C and heat treatment for 30 minutes were carried out. The wafer was ****(ed) and the cross section of a pattern was observed by one 10,000 times the scale factor of this using the scanning electron microscope (Akashi factory SIGMA-1 mold). The thickness C_{mum} of the insulator layer of the a total of B micrometers and the space section of the thickness A_{mum} of a 0.8-micrometer line and the line in the space section, the thickness of a line, and the thickness of the insulator layer formed in the upper part was measured among those, and whenever [flush-ized] was computed by $=1 - \{(B-C) / A\}$ whenever [formula [flush-ized]].

[0046] Example 1 dimethyl dimethoxysilane 72g, methyl trimetoxysilane 163g, and tetramethoxy silane 182g were put into 1l. flask with an agitator, and it was slowly dropped at 25 degrees C, having applied [7g of 0.1 N-HCl aqueous solutions, and / of 81g of water] them for 30 minutes. Furthermore, it let it pass in the column which mixed A101D with ion-exchange-resin Duolite C20, and the catalyst was removed. The weight average molecular weight of the obtained siloxane system prepolymer was 2500. Subsequently, isopropanol 800g was added and it considered as the spreading liquid for insulator layer formation. Subsequently, 0.5-N acetic acid / ethanol solution was added, and conductivity was adjusted to 5 second/cm. On 4 inch silicon BEAWEHA, this spreading liquid is changed, conditions are applied for it with a spin coat method, and it is 450 degrees C and N2. When heat treatment under an ambient atmosphere was performed, generating of a crack was not accepted by that to which the thickness after baking exceeds 1 micrometer, either. Next, when whenever [flush-ized] was measured using the silicon wafer with a pattern, whenever [flush-ized] was 0.90. Furthermore, although this spreading liquid was saved in the refrigerator (about 5 degrees C) for two months, whenever [flush-ized] is 0.90, and it turned out that it excels also in stability.

[0047] Like example of comparison 1 example 1, although the spreading liquid for insulator layer formation was created, adjustment of conductivity was not performed. The conductivity of spreading liquid was 0.01 second/cm. After what was 0.90 at the beginning saving in a refrigerator (about 5 degrees C) for one month, whenever [flush-ized] fell to 0.65 and the problem was in stability.

[0048] Like example of comparison 2 example 1, the spreading liquid for insulator layer formation was created, and conductivity was made into 200 second/cm. Although whenever [flush-ized] was 0.90 at the beginning, after saving in a refrigerator (about 5 degrees C), it fell to 0.70 for one month.

[0049] The monomer of the same presentation as example of comparison 3 example 1 was taught, and it was dropped slowly, having applied 7g of 0.1 N-HCl aqueous solutions, and the mixed liquor of 81g of water for 30 minutes at 40 degrees C, and stirring was further continued at 40 degrees C for 4 hours. Subsequently, it let it pass in the column which mixed A101D with ion-exchange-resin Duolite C20, the catalyst was removed, and the siloxane system prepolymer of weight average molecular weight 10,000

was obtained. Furthermore, isopropanol 800g was added and it considered as the spreading liquid for insulator layer formation, and when whenever [flush-sized] was measured, it became 0.60 and a low value.

[0050] Various additives for examples 2-8 and the example 4 of a comparison - 5 organic silicon compounds, a reaction condition, an organic solvent, conductivity, and conductivity adjustment (it is used as an ethanol solution) are changed, the spreading liquid for insulator layer formation is created, and the measurement result of whenever [in the conductivity and the wafer with a pattern of the weight average molecular weight of a prepolymer and spreading liquid / flush-sized] is shown in a table 3 and a table 4.

[0051]

[A table 1]

----- A fruit ** An example 1 2 3 4 5 6 7 organic silicon compounds Two functionality Class *1 MDM MDE MDM MDM MDE MDM EDE Amount g 7289 54 9089 36 79 A mole ratio 0.20 0.20 0.15 0.25 0.20 0.10 0.15 Three functionality Class *2 MTM MTE MTM MTM MTEETE PTM Amount g 163187 143102 187 230 297 Mole ratio 0.40 0.35 0.350.25 0.35 0.40 0.50 4 functionality Class *3 TM TE TE TE TM TMTM Amount g 182 281 312 312 205 228 160 Mole ratio 0.40 0.45 0.50 0.50 0.45 0.50 0.35 organic solvents Class *4 IPA EAC EAL EAL EAC IPA BAC Amount g 800800 800800 800800 800 weight average molecular weight 2500 2000 1500 3500 3000 4000 2500 additives Class *5 ACA AAC TAC ANI ACA NIA ACA conductivity mus/cm 5 3 2 1 10 0.820 ----- [0052]

[A table 2]

----- An example A ratio ** An example 8 1 2 3 4 5 organic silicon compounds Two functionality Class *1 EDE MDM MDM MDM The amount of MDE MDE g 158 72 72 72 89 89 A mole ratio 0.30 0.20 0.20 0.20 0.20 0.20 Three functionality classes *2 ETE MTM MTM MTM MTE MTE Amount g 202 163 163 163 187187 Mole ratio 0.35 0.40 0.40 0.40 0.35 0.35 4 functionality Class *3TE TMTM TMTE TE Amount g 281 182 182182 281 281 Mole ratio 0.350.40 0.40 0.40 0.45 0.45 organic solvent classes *4 EAL IPA IPA IPA EAC EAC Amount g 800 800 800 800 800 800 weight average molecular weight 2000 2500 2500 10000 2000 7000 additives Class *5 TCH - ACA ACA AAC AAC conductivity mus/cm 1 0.01 200 5 3003 ----- [0053]

[A table 3]

----- A fruit ** An example 1 2 3 4 5 6 Seven assessment Whenever [flattening] Immediately after production 0.90 0.90 0.90 0.85 0.85 0.80 0.851 months after 0.90 0.90 0.90 0.85 0.85 0.80 0.85 ----- [0054]

[A table 4]

----- An example A ratio ** An example 8 1 2 3 4 Five assessment Whenever [flattening] Immediately after production 0.90 0.90 0.90 0.60 0.90 0.65 One month after 0.90 0.65 0.700.60 0.65 0.65 ----- [0055]

*1 The class MDM:dimethyl dimethoxy run MDE:diethyl dimethoxy run EDE of 2 functionality organic silicon compound : diethyl diethoxy run [0056]

*2 Class MTM:methyl trimetoxysilane MTE:methyl triethoxysilane ETE:ethyltriethoxysilane PTM of 3 functionality organic silicon compound : phenyl trimethoxysilane [0057]

*3 The class TM:tetramethoxy silane TE of 4 functionality organic silicon compound : tetra-ethoxy silane [0058]

*4 class IPA:isopropanol EAC:ethyl-acetate EAL:ethanol BAC: of an organic solvent -- butyl acetate [0059]

*5 Class AAC:ammonium acetate TAC:acetic-acid tetramethylammonium ANI of an additive : ammonium-nitrate ACA:acetic-acid NIA:nitric-acid TCH:carbonic acid hydrogen tetramethylammonium [0060]

[Effect of the Invention] By this invention, also as for the narrow pattern, whenever [flattening] was good, and it was able to offer the spreading liquid for silica system insulator layer formation excellent in stability with the passage of time as explained above.

[Translation done.]